The path integral formulation of a polymer chain with stiffness and its phase transitions : Analytic theory of DNA condensation(Soft Matter as Structured Materials)

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— Analytic theory of DNA condensation —

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完全屈曲性高分子鎖の連続理論は、場の理論による相転移の記述等よく知られている。一方、より一般の半屈曲性高分子鎖については、MD 法やモンテカルロ計算で一定の理解は得られたが、予言性を持つ解析理論に至っていない。我々はこのモデルを経路積分において引力項付きで定式化し、DNA 凝縮に特徴的なトロイド状態を導出した。更にウィップ - トロイド相転移等を議論する。

As simple models of DNA condensation [1], semiflexible homopolymers in a poor solvent condition have been much investigated by simulations using Monte Carlo, Langevin approaches or Gaussian variational method for its phase diagram [2], and by theoretical works estimating such toroidal properties [3]. It becomes increasingly probable that toroid is the ground state. However in the theoretical side, they assume a priori toroidal geometry as the stable lowest energy state. Compared to the theory of coil-globule transition of flexible chains [4, 5], which are well described by field theoretical formalism [4], there is no simple microscopic theory, which demonstrates whip-toroid transition of the semiflexible polymer [6]. In this talk, we show such a transition using path integral method and the nonlinear sigma model on a line segment.

In the continuum limit, the Green function of a stiff polymer chain with attractive interactions can be given by the path integral with a constraint $|\vec{u}|^2 = 1$ [6]:

$$G(\vec{0},\vec{R};\vec{u}_i,\vec{u}_f;L,W) = \mathcal{N}^{-1}\int_{\vec{r}(0)=\vec{0},\vec{u}(0)=\vec{u}_i}^{\vec{r}(L)=\vec{R},\vec{u}(L)=\vec{u}_f} \mathcal{D}[\vec{r}(s)]\, e^{-\mathcal{H}[\vec{r},\vec{u},W]}. \tag{1}$$

s is the proper time along the chain of length L. $\vec{r}(s)$ is the 3-d pointing vector at s while $\vec{u}(s) \equiv \frac{\partial \vec{r}(s)}{\partial s}$ is the unit orientation vecotor at s. $\mathcal{N}$ is the normalisation constant. The dimensionless Hamiltonian can be written by $\mathcal{H}[\vec{r},\vec{u},W] = \int_0^L ds\, [H(s) + V_{AT}(s)]$ with $H(s) = \frac{l}{2}\left|\frac{\partial}{\partial s}\vec{u}(s)\right|^2$, $V_{AT}(s) = -W\int_0^s ds'\delta(\vec{r}(s)-\vec{r}(s'))$. l is the persistence length and W is a positive coupling constant of attraction between polymer segments. The Boltzmann weight is implicit.

Our Hamiltonian with the constraint $|\vec{u}(s)|^2 = 1$ can be interpreted as the low energy theory of the $O(3)$ nonlinear sigma model on a line segment. The constraint $|\vec{u}|^2 = 1$ in $\mathcal{H}(\vec{u}) =$

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$\frac{l}{2}\int_0^L ds\ |\partial\vec{u}(s)|^2$ in the polar coordinates gives

$$\mathcal{H}_{bending} = \frac{l}{2}\int_0^L ds\ \left[(\partial\theta_u)^2 + \sin^2\theta_u(\partial\varphi_u)^2\right]. \tag{2}$$

By solving the classical equations of motion, we obtain two types of classical solutions such as $\vec{u}(s) = const.,\ \ or\ \ \theta = \frac{\pi}{2}\ and\ \varphi_u = as + b$ where a, b are constants. Introducing the winding number of the solutions $N(s) \equiv [as/2\pi]$ with Gauss' symbol, we obtain their Hamiltonian:

$$\mathcal{H}_{cl}(a, l, L, W) \equiv \frac{Ll}{2}a^2 + \frac{\pi W}{a}N(L)\left(N(L)+1\right) - WL\cdot N(L). \tag{3}$$

The non-zero winding number of the classical solution in the $\vec{u}$ space means a "Toroid state" of radius $1/a$ which stabilises itself by attracting neighbouring segments. When $0 < a \leq \frac{2\pi}{L}$, as long as the total energy of the chain does not exceed the bending energy of $\frac{2\pi^2 l}{L}$, they can whip with zero winding number. We call such low-energy states "Whip states."

By rewriting the above form as follow, one can easily see that the functional shape of the energy level is governed by the value $c \equiv \frac{W}{2l}\left(\frac{L}{2\pi}\right)^2$

$$\mathcal{H}_{cl}(a, l, L, W) = \frac{WL}{2}\mathcal{H}(c, x)\ \ where\ \ \mathcal{H}(c, x) = \frac{x^2}{2c} + \frac{1}{x}[x]([x]+1) - 2[x], \tag{4}$$

with a new variable $x \equiv \frac{aL}{2\pi}$, $[x] = N(L)$. By plotting this with different values of c, one can find that there is a critical value $c = \frac{1}{2}$ where the meta-stable state with $N(L) = 1$ vanishes. This is a critical point where the phase transition from a Toroid state to a Whip state is accomplished.

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